THE HIGH RESOLUTION RAMAN SPECTRA OF THE ν_4 BAND OF DIBORANE

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Diborane is the simplest of the boro-hydride compounds containing a bridge-hydrogen structure. We report here a study of the high resolution gas phase Raman spectrum of the B$\cdots$B stretching band, ν_4 (A_g), of this interesting near-prolate asymmetric rotor molecule. The sample contained boron in natural abundance, and therefore, the following isotopomers were present: $^{11}B_2H_6$ (64%), $^{10}B^{11}BH_6$ (32%), and $^{10}B_2H_6$ (4%). The symmetry of the two symmetric isotopomers is D_{2h} while the other species has C_{2v} symmtery. The isotopic shift for this vibration is large, however, and the spectra of the two most abundant isotopic species were isolated and recorded. Spectra were recorded with the high resolution inverse Raman spectrometer at Madrid, with an instrumental resolution of ~ 0.003 cm^{-1} and accuracy of ~ 0.001 cm^{-1}. The cell was filled with 10 mbar of diborane and packed in dry ice, and a triple pass configuration was used to enhance the rather weak signal.

The analysis of the spectrum was not straightforward. For this totally isotropic vibration almost all the band intensity is found in the ^qQ-branch since the P- and R-branch transitions are 1 to 2 orders of magnitude weaker in intensity and were not observed in this study. As a result, it was not possible to use combination differences to verify the line assignments. Moreover, the vibrational change in the value of the A rotational constant is small (~ -0.0022 cm^{-1}); accordingly, the ^qQ_K sub-branches are completely overlapped, and very few isolated lines are found in the spectrum. However, by fitting higher J-K_a transitions, an estimate of the upper state rotational conants was obtained, which was refined in an iterative process by comparing simulated and observed spectra. For the spectrum of the $^{11}B_2H_6$ species, a slightly improved fit was obtained by invoking a weak resonance with the $2\nu_{10}$ state. The band centers obtained were 790.9829(12) cm^{-1} and 804.76985(27) cm^{-1} for $^{11}B_2H_6$ and $^{10}B^{11}BH_6$, respectively.

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